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Apta-nanosensors for detection and quantitative determination of acetamiprid – A pesticide residue in food and environment

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ABSTRACT

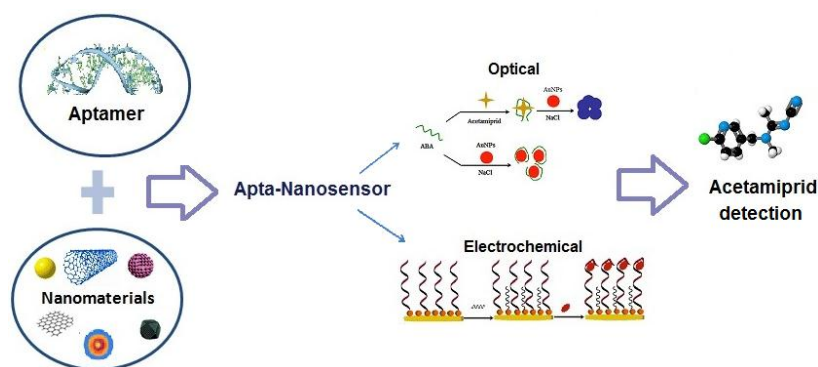
In an effort to achieve high sensitive and selective detection of pesticide residues, numerous nanomaterial-based aptasensors are currently being developed for acetamiprid analysis. Recently, aptamers as a potent alternative of antibodies are used in biosensing platforms. There is tremendous interest in utilizing of nanomaterial as basic building blocks and signaling elements in aptasensors. The nanomaterials have the unique optical and electrical properties. The combination of nanomaterial and aptamer technology has opened a new window in pesticide residues monitoring. In this review, recent advances and applications of optical and electrochemical nanomaterial-based aptasensors for the detection and quantitative determination of acetamiprid in details have been discussed.

Abbreviations

ABA, acetamiprid-binding aptamer; Au NRs, Au nanorods; CB, conduction band, CdTe; CL, chemiluminescence; CNTs, carbon nanotubes; CS, complementary strand; Cy5.5, Cyanine5.5; DPV, differential pulse voltammetry; dsDNA, double stranded DNA; EDC, ethyl(dimethylaminopropyl) carbodiimide; EIS, electrochemical impedance spectroscopy; Exo I, Exonuclease I; FRET, fluorescence resonance energy transfer; GNPs, gold nanoparticles; ITO, Indium tin oxide; LOD, limit of detection; RET, resonance energy transfer; R_{et} , electron transfer resistance; rGO, reduced graphene oxide; RLS, resonance light scattering; MB, methylene blue; MCH, 6-mer-capto-1-hexanol; MWCNTs, multi-walled carbonnanotubes; NHS, N-Hydroxysuccinimide; NPs, nanoparticles; PEC, photoelectrochemical; QDs, quantum dots; SiNP, silica nanoparticles; SPR, surface plasmon resonance; SWNTs, single-walled nanotubes; S-18

aptamer, acetamiprid-specific aptamer; TMB, 2, 3,3,5,5-tetramethylbenzidine; TMB_{OX}, oxidized TMB; UCNPs, upconversion nanoparticles; VB, valence band

Graphical Abstract



Keywords: nanomaterials; acetamiprid; aptamer; biosensor

1. Introduction

Pesticide residue detection is a main concern of food safety experts, and a rapid pesticide residue detection method is needed to keep humans from being affected. Acetamiprid is a broad-spectrum and contact insecticide that is widely used as replacement insecticide of organophosphorus and other conventional insecticides to control sucking-type insects on various crops, especially leafy vegetables, fruits and tea trees [1, 2]. Despite the relatively low mammalian toxicity and special acting characteristics, acetamiprid can generate potential health risk of human beings, who are exposed to the food and environments polluted [3]. Using of acetamiprid has been banned in many countries, because of severe environmental pollution and pesticide-resistance [4]. Therefore, the sensitive and selective tracing of this nerve poison has become critical for human and environmental health. To date, contemporary pesticide detection methods such as high pressure liquid chromatography (HPLC) [5], mass spectrometry (MS) [6], gas chromatography (GC) [7], flow and antibody-based immunoassays (AIA) [8, 9] schemes have been used in the detection of acetamiprid. However, these conventional methods are intricate and time consuming and also often need expensive equipments, making such approaches impractical for on-site and regular environmental monitoring. Therefore, it is necessary to develop simple, sensitive, rapid, cost-effective, and field-portable alternatives for acetamiprid determination in order to reduce the risk to

public health. Biosensors are considered to be promising tools for monitoring food and environment pollution. Biosensors are rapid, cost-effective, field-portable and high-sensitivity instruments, which can detect and measure targets by transforming the recognition of targets into a physically detectable signal, such as optical, electronic or magnetic signals [10-12]. The latest of the biosensors for detection of acetamiprid are aptasensors, which use aptamer as a reorganization element [13]. Aptamer is a single-stranded oligonucleotide that folds into distinct conformation capable of binding strongly and selectively to a target [14, 15]. These synthetic oligonucleotides are promising probes to be used for fabrication of a wide range of aptamer-based biosensors. Aptamers are synthesized by an in vitro and cost effective process called SELEX (Systematic evolution of ligands by exponential enrichment) [16, 17]. Compared to antibody-based biosensors, aptasensor possess outstanding features, such as high productivity, affinity, selectivity, and stability [18-20]. An aptasensor is a kind of biosensor which the biological recognition element is a DNA or RNA aptamer.

Recently developments in nanotechnology show the potential of nanoparticles as the basic building blocks and signaling elements for fabrication of biosensors with excellent performance [21-23]. Nanoparticles exhibit unique optical and electrochemical properties with various functions, including targeting, sensing and imaging [24]. They have large surface area, nano scale size and unique morphology which are utilized in different sensing methods such as optical, electrochemistry, surface plasmon resonance (SPR), and catalytic activity. In recent years, different nanomaterials such as metallic nanoparticles (NPs), quantum dots (QDs), carbon nanotubes (CNTs) and silica (SiO₂) NPs are used with aptamers in biosensor designing [25-28]. It opened a new opportunity for introducing novel nanomaterial-based aptasensors for specific and sensitive molecular detection. The nanomaterial-based aptasensors successfully detect a number of pesticide residues of interest by taking advantages of high amplification of signals [29-34]. Herein, a review has been provided with special emphasis on the recent advances in aptasensors developed for acetamiprid detection in order to provide an understanding of its improvement and progress.

2. Acetamiprid aptasensors

Some detection approaches have been used for acetamiprid aptasensors. These are divided into two classes: optical and electrochemical. Among them, the former is interested a lot because of their inherent advantages such as simplicity, high sensitivity and low cost. Optical aptasensors can be

divided into subclass: absorption, fluorescence, colorimetric and chemiluminescence methods. In this section the highlights and different examples of acetamiprid optical aptasensors were summarized.

3. Optical aptamer-based acetamiprid biosensors

3.1. Colorimetric-based aptasensors

Colorimetric sensors for real-time naked-eye detection have attracted much regard due to its low cost, simplicity, label-freeness and practicality can be performed without the presence of trained technician or precise instrument [35].

Gold nanoparticles (GNPs) have been extensively used to develop the colorimetric aptasensors, according to their unique optical properties such as large surface area, high extinction coefficient, well biocompatibility, excellent signal-to-noise ratio, ease of synthesis and peroxidase-like activity [36, 37]. Shi et al. [38] presented the first colorimetric aptasensor for acetamiprid detection by using GNPs (Fig. 1).

Fig. 1:

In the absence of acetamiprid, aptamer could serve as a stabilizer and protect GNPs from salt-induced aggregation, leading to the color of Au-NPs remained red. Upon addition of acetamiprid, the aggregation of GNPs happened, resulting in the formation of purple blue color. The practical application of this assay was realized for detecting acetamiprid in real soil samples.

Some unique nano-materials have inherent peroxidase-like activity which offers new opportunities for biosensor development, as this nanozyme activity [39, 40]. In this fact, Weerathunge et al. [29] presented a colorimetric aptasensor for the detection of acetamiprid by employing gold nanozyme activity (Fig. 2). In this assay, GNP surface was shielded by the aptamer and its nanozyme activity inhibited. In the presence of acetamiprid, the aptamer undergoes conformational changes and resulting in free GNP to resume its peroxidase like activity.

Fig. 2:

Similarly, in one of the reports, based on peroxidase-like activity of hemin-functionalized reduced graphene oxide (rGO), a colorimetric aptasensor was developed for acetamiprid detection with LOD of 40 nmol L⁻¹ by Yang and coworkers (Fig. 3) [41]. The hemin-functionalized rGO composite peroxidase-like activity was blocked by absorbed aptamers. In the presence of the acetamiprid, the aptamer on the nano-composite released and the peroxidase-like activity was recovered and could be measured the acetamiprid concentration.

Fig. 3:

In a very recent attempt, Tian et al. [42] demonstrated that truncated 37-mer and 25-mer aptamers improve colorimetric sensitivity for acetamiprid detection by 3.3-fold compared with the 49-mer. When the target is exposed to long sequence aptamer, the bases outside of the binding region of aptamer may still adhere to GNPs, which prohibits GNPs from aggregation but the short aptamer may dissociate from GNPs completely.

3.2. Fluorescence-based aptasensors

Fluorescence analysis is one of the most popular optical techniques in aptasensor designs because of its particular characteristics including high sensitivity, high efficiency, simplicity and rapid analysis [43]. Quantum dots have been used as excellent nano-fluore tags in aptasensing owing to their unique properties include high quantum yield, stable fluorescence, symmetric and narrow emission band and broad absorption spectra [44-47].

Guo and colleagues designed a fluorescence aptasensor to detect acetamiprid based on CdTe quantum dots fluorescence quenching with GNPs by the inner filter effect (IFE) [48]. In this assay, the IFE efficiency could be readily modulated by the absorption and the aggregation state of GNPs. The adding of salt could induce the aggregation of GNPs and the fluorescence recovery of the quenched QDs. Aptamer could protect the GNPs from salt-induced aggregation, so the fluorescence of QDs would be quenched by the IFE of GNPs. In the presence of acetamiprid the aptamer preferentially bounded to its target, so aptamers release from GNPs. Therefore, the IFE-decreased fluorescence of QDs was tacked back with the presence of acetamiprid (Fig. 4).

Fig. 4:

Lin and coworkers used switch-on fluorescent scheme for the acetamiprid detection [49]. In this report, authors designed a new biosensor based on QDs functionalized with aptamer. The fluorescence of the QDs was quenched by multi-walled carbonnanotubes. Upon acetamiprid addition, a structural switch of the aptamer caused the release of the MWCNTs and a simultaneous increase in fluorescence signal on the QDs. The proposed aptasensor was successfully applied to measure acetamiprid in real water samples.

Xiang and coworker used fluorescence resonance energy transfer (FRET) scheme for the acetamiprid detection [50]. In this FRET aptasensor QD used on complementary aptamer as donor and a fluorescent dye on aptamer as the acceptor. In the presence of acetamiprid, the specific interaction between the aptamer and target prevented the vicinity of the donor and acceptor, so the energy transfer efficiency decreased. This FRET aptasensor was well qualified acetamiprid in spiked water samples with high recovery.

In recent years, there has been considerable interest in to upconversion nanoparticles in different fields [51-53]. UCNPs exhibit unique properties, including photo-stability, low toxicity, narrow emission spectrum and low background fluorescence [54-56]. Thus, UCNPs have great promise for biosensors based on fluorescence labeling and are widely used as novel.

Hu and co-workers presented a sensitive FRET-based aptasensor for the detection of acetamiprid by using the UCNPs as donor and the GNPs as acceptor [57]. The aggregated GNPs could not quench the fluorescence of UCNPs, on the other hand, the GNPs which protected by aptamers were able to efficiently quench the fluorescence of UCNPs (Fig. 5). The detection limit of the assay was measured to be 3.2 nmol L^{-1} .

Fig. 5:

Silica nanoparticles have recently obtained remarkable attention for biosensing applications, according to their unique properties such as ease of synthesis, stability, low-cost, no toxicity and good biocompatibility [58-60]. SiNP can increase fluorescence intensity by virtue of optical interference [61, 62].

Abnous et al. [63], reported a fluorescence aptasensor using nanoparticles for signal amplification of fluorophore (FAM) with a limit of detection as low as 127 pM. The authors used three kinds of nanoparticles (SiNP, GNPs and carbon nanotubes) with contrary effects on the FAM (Fig. 6).

Fig. 6:

In the presence of acetamiprid, the aptamer on SiNP preferentially bounded to its target, so FAM-labeled complementary strand (CS) release to the supernatant (phase I). Phase I is reach of FAM-labeled CS and its fluorescence intensity decreases by adding to phase II (the SWNTs and GNPs as quenchers). In the absence of target, the dsDNA-modified SiNP remains intact and no labeled CS is present in the phase I. Therefore, very weak relative fluorescence intensity was observed.

3.3. Chemiluminescence-based aptasensors

Chemiluminescence is the emission of luminescence as a result of multi-step oxidation reactions with fast reaction kinetics. The unique characteristics of CL contain high sensitivity, wide calibration ranges, simple operation and short assay time.

The catalytic activity of aggregated GNPs for the luminol–H₂O₂ CL reaction is stronger than that of dispersed GNPs [64-66]. In this fact, Qi et al. reported a CL aptasensor for acetamiprid detection with LOD of 62 pmol L⁻¹ (Fig. 7) [67]. In the presence of target, the aptamer preferentially bound with acetamiprid and could not protect GNPs from salt induced aggregation. This morphology of GNPs exhibited super strong catalytic performance. This CL assay was successfully used to determine acetamiprid in real samples.

Fig. 7:

3.4. Resonance light scattering (RLS)-based aptasensors

The resonance light scattering as a sensitive and simple analysis technique can provide insights into the treatment responsible for the formation of an aggregate type of structure [68]. Wang et al. presented a RLS aptamer-based biosensor for acetamiprid detection by using GNPs [69]. Without acetamiprid, GNPs were stabilized from salt induced aggregation by aptamers. When the target was introduced into the biosensor, the aptamer bind to target with high affinity and aggregation of GNPs caused the RLS signal intensity to be enhanced. This aptasensor exhibited the LOD as low as 1.2 nmol L⁻¹ and used for lake water sample analysis. The progress that has been made in aptamer-

based optical detection of acetamiprid has been summarized. These aptasensors have been listed in Tables 1.

Table 1:

4. Electrochemical aptamer-based acetamiprid biosensors

Among the various aptasensors, electrochemical aptasensors are interested a lot because of their inherent advantages such as simplicity, high sensitivity, rapid response, low cost and high stability [71, 72].

Fan and coworkers used electrochemical impedance spectroscopy for acetamiprid detection (Fig. 8) [73]. Authors improved the sensitivity of the aptasensor by GNPs electrodeposition on the work electrode surface. In the presence of analyte, because of the formation of aptamer/target couple, the electron transfer resistance (R_{et}) increased which was quantified by EIS. The designed aptasensor has been successfully evaluated by detection acetamiprid in the wastewater and tomatoes samples.

Fig. 8:

In a similar study, Fei et al. improved the sensitivity of the aptasensor as low as femtomole level by using gold nanoparticles decorated multiwalled carbon nanotube-reduced graphene oxide nanoribbon composites [74]. This developed impedimetric aptasensor was successfully used to detect acetamiprid in water samples.

Similarly, Jiang and coworkers designed an impedimetric aptasensor to detect acetamiprid by same sensing scheme, but in this assay silver nanoparticles anchored on nitrogen-doped graphene as a novel electrochemical biosensing platform was used as signal amplification [75]. Resulting aptasensor could analysis acetamiprid as low as 3.3×10^{-14} mol L⁻¹ and in real samples from environment and food.

An electrochemical assay, based on aptamer, polyaniline film and GNPs was established for the specific detection of acetamiprid with LOD of 0.086 μ M by Rapini and coworkers [76]. In this platform, graphite screen-printed electrode modified with polyaniline film and GNPs and then thiolated aptamer was immobilized. After competitive reaction between acetamiprid and complementary sequence (oligo2) for binding to the aptamer, streptavidin-alkaline phosphatase enzyme conjugates to oligo2 (Fig. 9). A decrease of the current peak height was recorded increasing

the concentration of the acetamiprid at fixed concentration of oligo2. The assay was applied to analyze spiked acetamiprid in fruit juice samples.

Fig. 9:

Taghdisi et al. developed an aptasensor for acetamiprid detection based on target-induced redox probe release [77]. In this biosensing method, silica nanoparticles were coated with dsDNA formed between aptamer and complementary strand (Apt/CS) and the redox probe methylene blue intercalated in dsDNA. In the presence of acetamiprid, MB is released from the dsDNA and after CS digesting by Exo I, MB is detected electrochemically using an unmodified gold electrode (Fig. 10). Moreover, the developed electrochemical aptasensor could well detect acetamiprid in water and serum with LODs of 161 and 209 pmol L⁻¹, respectively.

Fig. 10:

4.1. photoelectrochemical-based aptasensors

PEC sensors are solar cells and created on photoactive electrodes which can convert photo irradiation to electrical response. Owing to the abilities of high sensitivity, simple equipment, ease of miniaturization, and cost-effectiveness, PEC sensors have attracted increasing research interest in recently [78].

Li et al. took use of Co-doped ZnO diluted magnetic semiconductor nanoparticles and constructed a PEC aptasensor for acetamiprid [79]. The aptamer was immobilized on the surface of Co-doped ZnO photoanode. In the presence of acetamiprid, the target could react with the aptamer which induces the decrease of enhanced photocurrent produced by the electron donor of quercetin (Fig. 11). This aptasensor exhibited the LOD as low as 0.18 nmol L⁻¹ and were used for cucumber sample analysis.

Fig. 11:

Liu and co-workers presented a sensitive resonance energy transfer-based aptasensor for the detection of acetamiprid by using the CdTe quantum dots as donor, gold nanorods as acceptor and MWCNTs/rGO nanoribbons as efficient signal amplifier (Fig. 12) [80]. In the presence of acetamiprid, the aptamer release from the electrode surface, and thus the low loading of the energy

acceptor Au NRs and thus increased the PEC signal. This “on-off-on” aptasensor has been successfully applied to analyze acetamiprid in apple and tomato samples.

Fig. 12:

A summary of the reports on acetamiprid aptasensors based on electrochemical methods are listed in Table 2.

Table 2:

5. Conclusions and perspectives

Pesticide residue is one of the main concerns in food safety and environmental pollution, and it is essential to establish an efficient and reliable method to quantify this residues. Herein, the advances have been made so far regarding nanomaterial-based aptasensors for acetamiprid detection using both optical and electrochemical analysis strategies has been summarized. The range of examples presented in this review demonstrates that combination of nanomaterial and aptamer technology will be an excellent and novel biosensing platform for acetamiprid detection by the unique optical and electrical properties of nanomaterials and highly selective interactions of the aptamer and its target. The optical assay is utilized a lot because of its inherent advantages. Fluorescence, colorimetry and chemiluminescence have opened promising optical approaches for acetamiprid detection. Recent progress in electrochemical nano-aptasensors has represented their ability to acetamiprid monitoring by high sensitivity as low as femtomole level. Despite all developments in acetamiprid aptasensors, very few commercial products are available. With advances in nanosciences, the novel aptasensing technologies would have the potential to be marketed in the near future for food and environment monitoring. Therefore, future research efforts should be focused on construction commercial nano-aptasensors.

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Figure captions:

Fig. 1. Colorimetric method for detection of acetamiprid based on GNPs and aptamer. Reproduced from Ref. [38], with permission from Elsevier.

Fig. 2. Scheme of depicting the acetamiprid colorimetric aptasensor based on peroxidase-like activity of GNPs. Adapted from the published works of [29], with permission from American Chemical Society.

Fig. 3. Scheme of the working principle for the colorimetric aptasensing of acetamiprid. A Reproduced from Ref. [41], with permission from Elsevier.

Fig. 4. Schematic illustration of the fluorescent sensing for acetamiprid based on the inner filter effect of GNPs on the fluorescence of QDs. Reproduced from Ref. [48], with permission from Springer.

Fig. 5. A FRET-based probe for the detection of acetamiprid. Reproduced from Ref. [57], with permission from Elsevier.

Fig. 6. Schematic illustration of acetamiprid detection based on fluorescent method. Reproduced from Ref. [63], with permission from Springer.

Fig. 7. Schematic illustration of the CL aptasensor for acetamiprid detection. Reproduced from Ref. [67], with permission from Elsevier.

Fig. 8. Illustration of the impedimetric aptasensor fabrication for acetamiprid detection. Reproduced from Ref. [73], with permission from Elsevier.

Fig. 9. The stepwise preparation of the electrochemical aptasensor for acetamiprid detection. Reproduced from Ref. [76], with permission from Elsevier.

Fig. 10. Schematic illustration of electrochemical sensing of acetamiprid based on target-induced strand release mechanism. Reproduced from Ref. [77], with permission from Springer.

Fig. 11. Schematic representation of the prepared PEC aptasensor for acetamiprid detection. Reproduced from Ref. [79], with permission from Elsevier.

Fig. 12. Schematic illustration of the prepared PEC aptasensor for acetamiprid detection based on the RET from CdTe QDs to Au NRs. Reproduced from Ref. [80], with permission from Elsevier.

Figures:

Figure 1

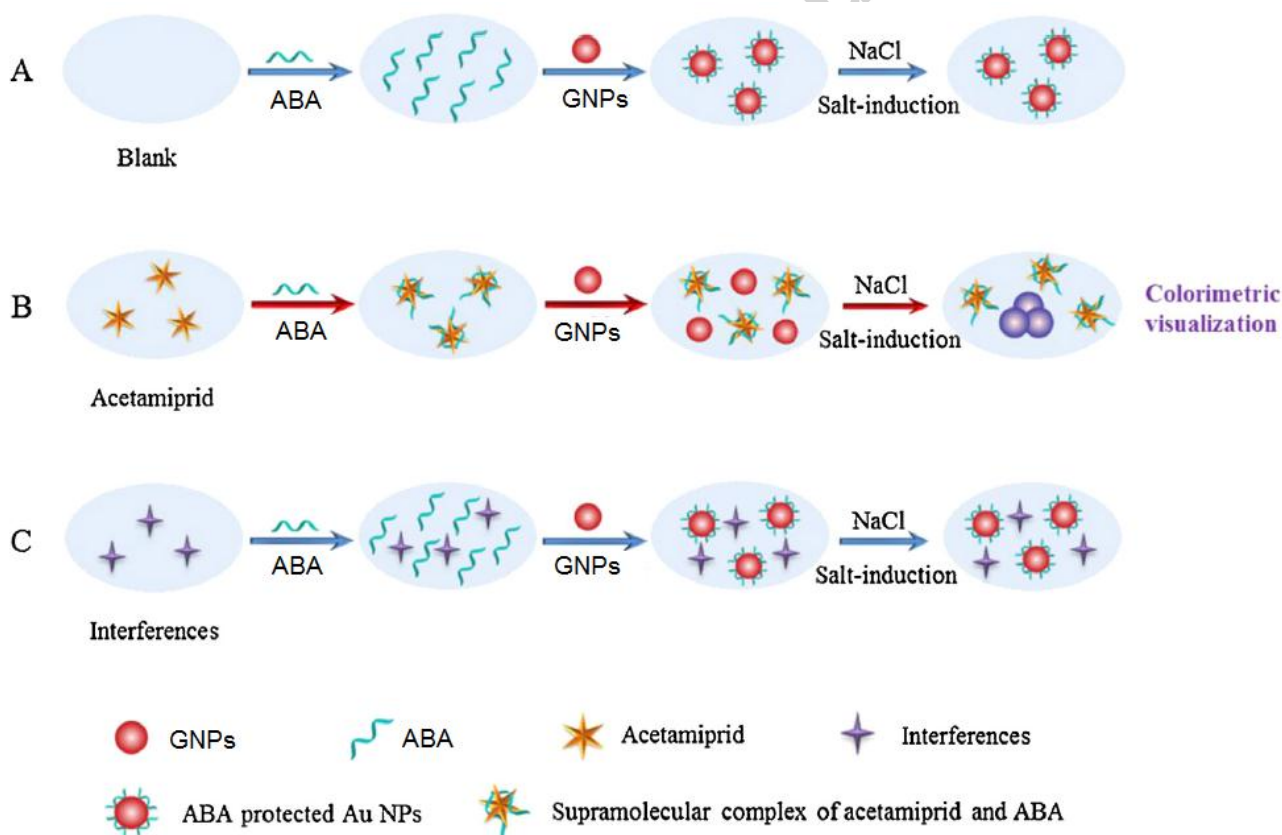


Figure 2

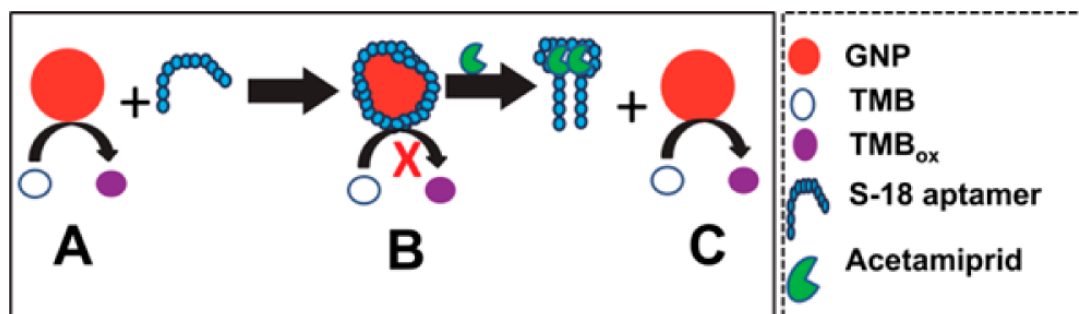


Figure 3

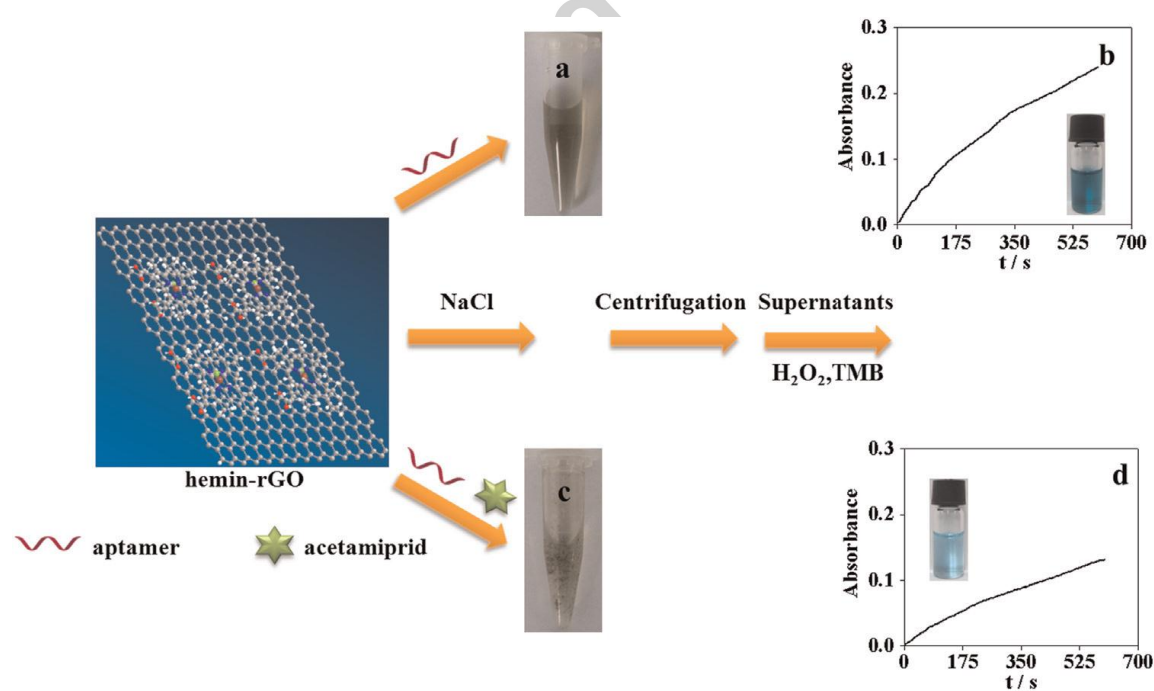


Figure 4

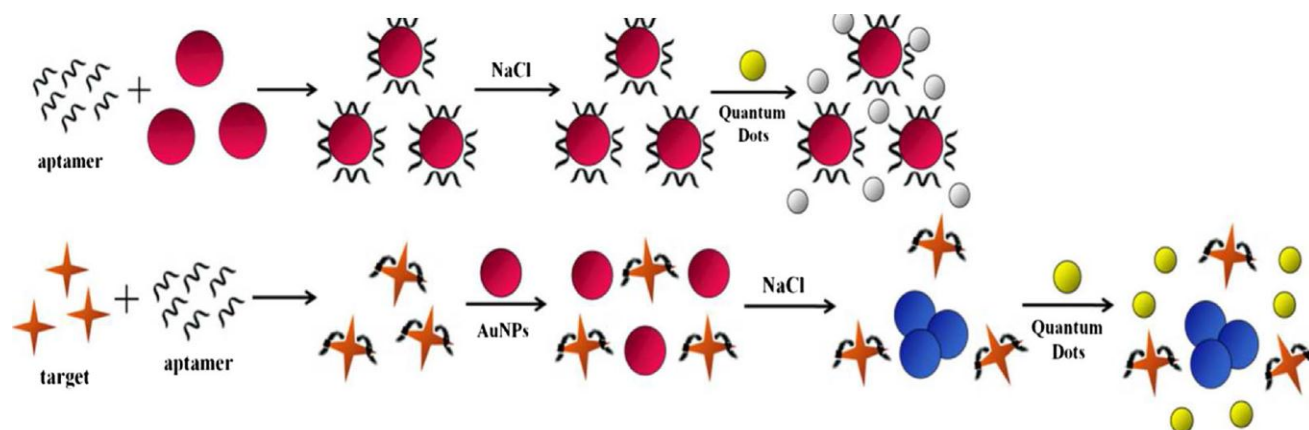


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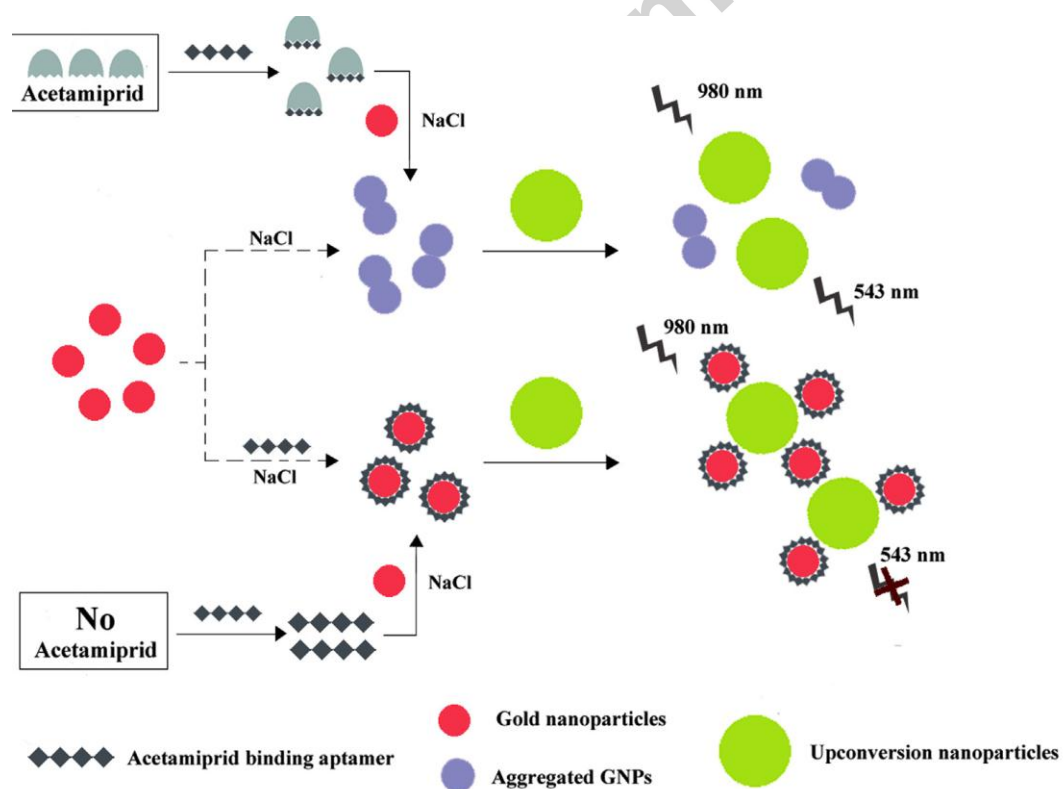


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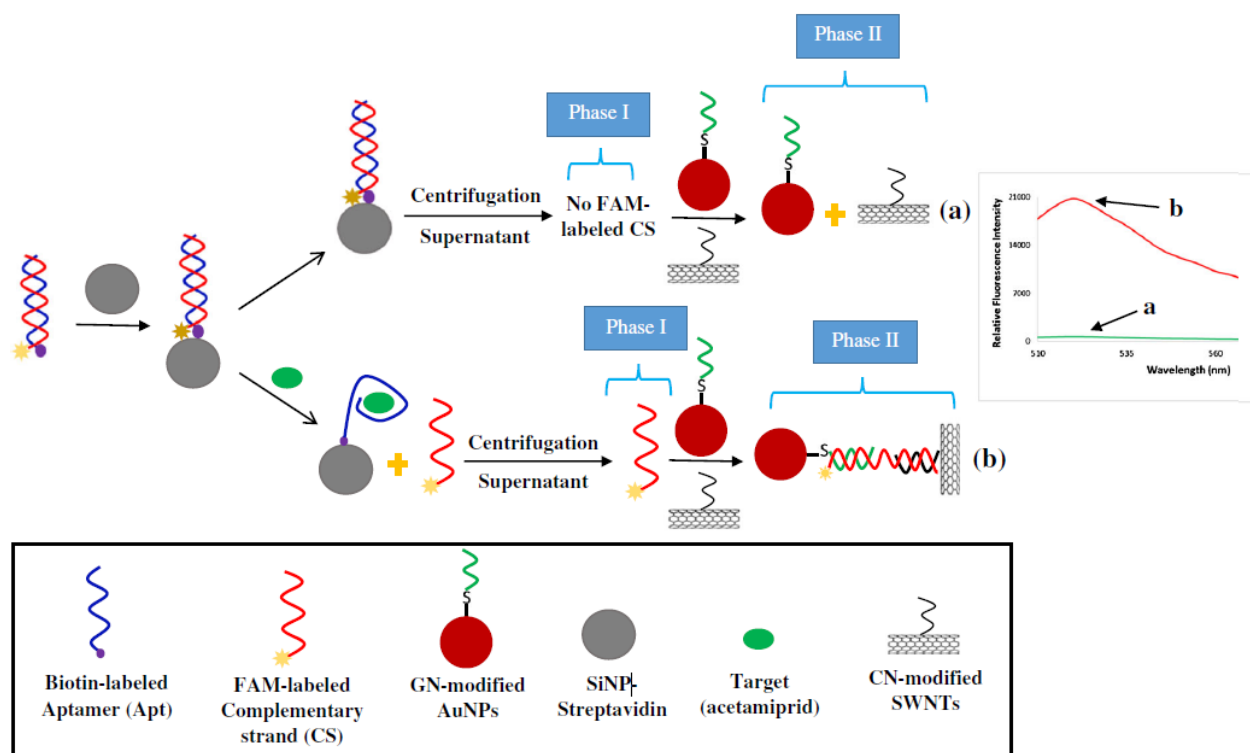


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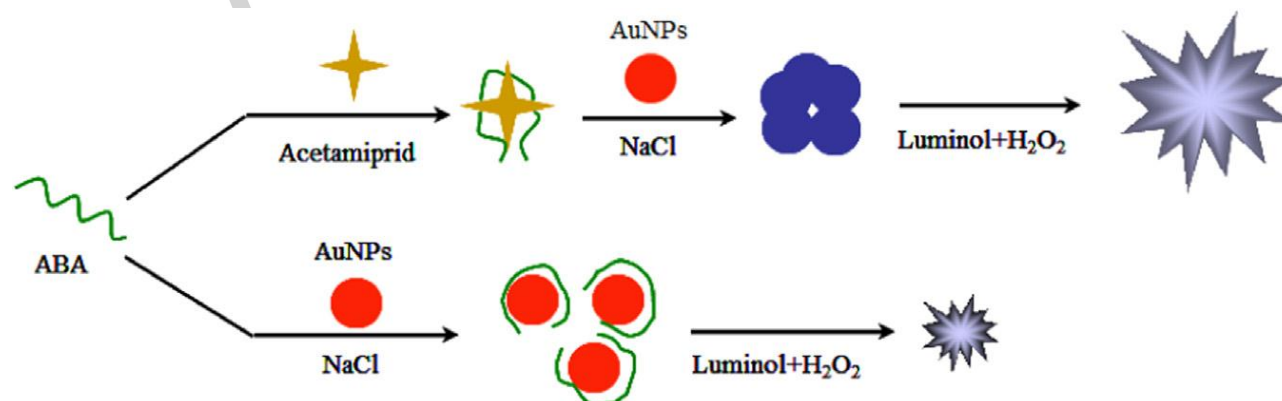


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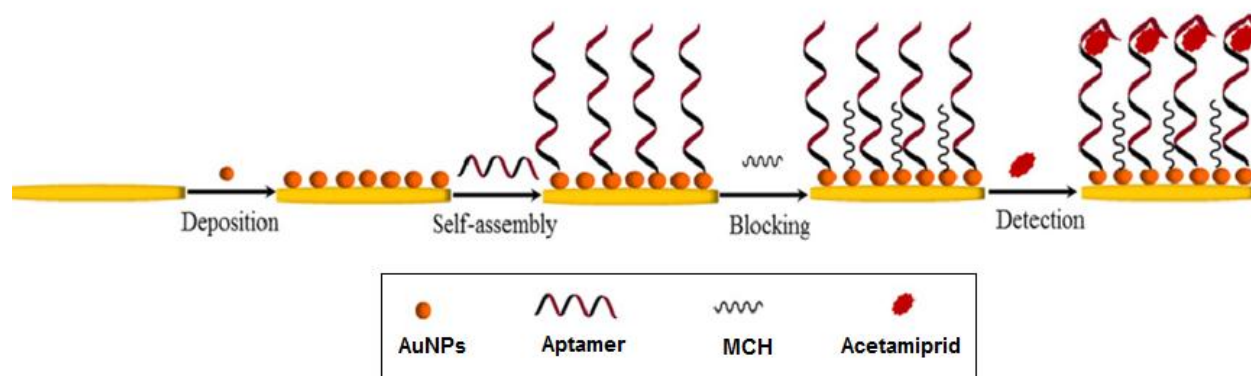


Figure 9

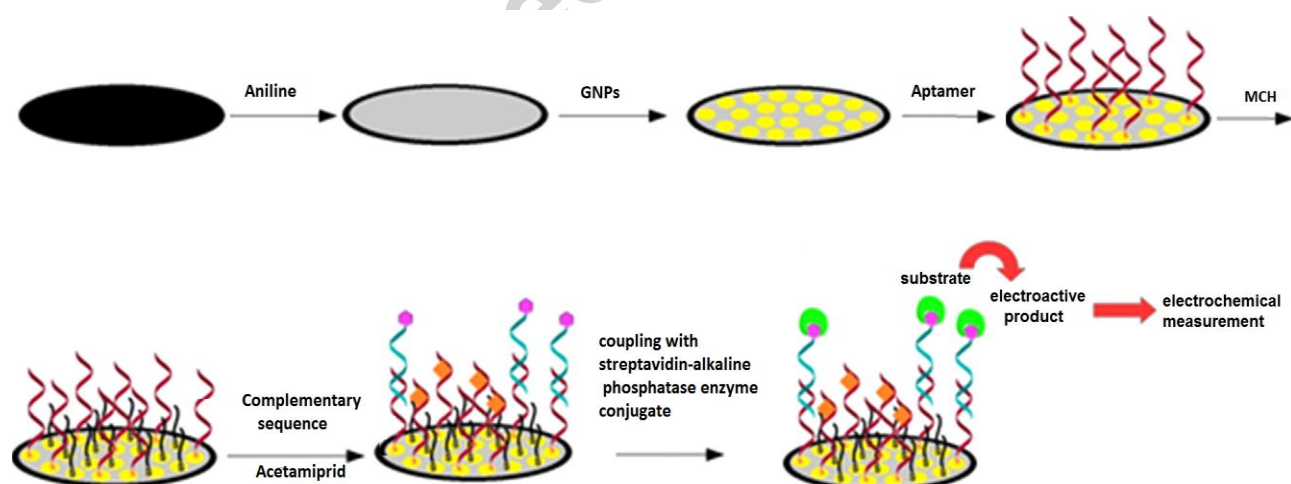


Figure 10

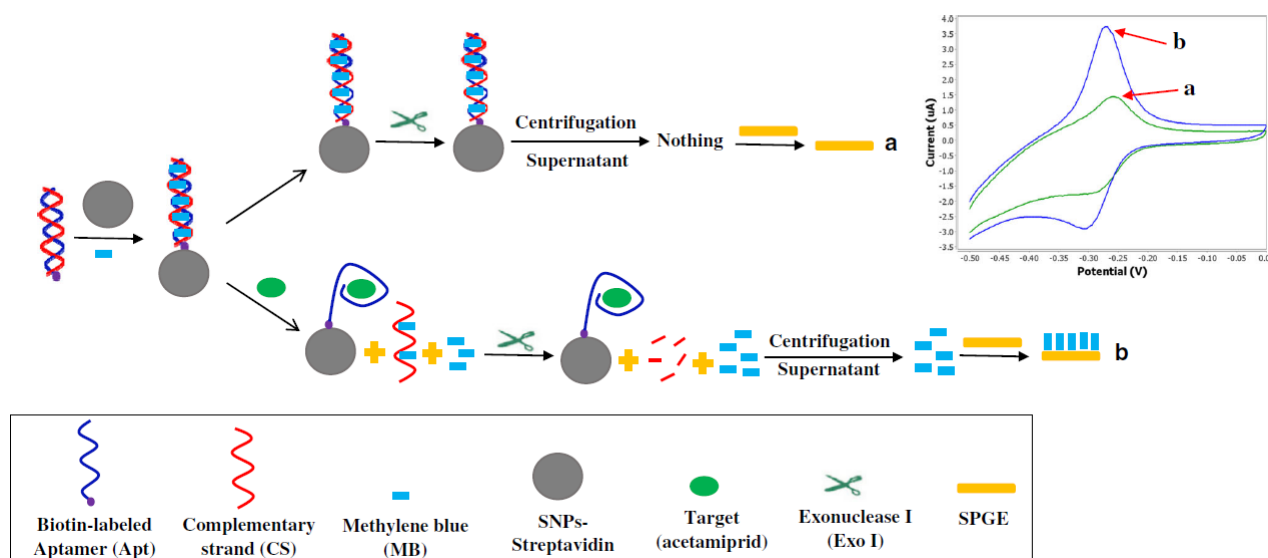


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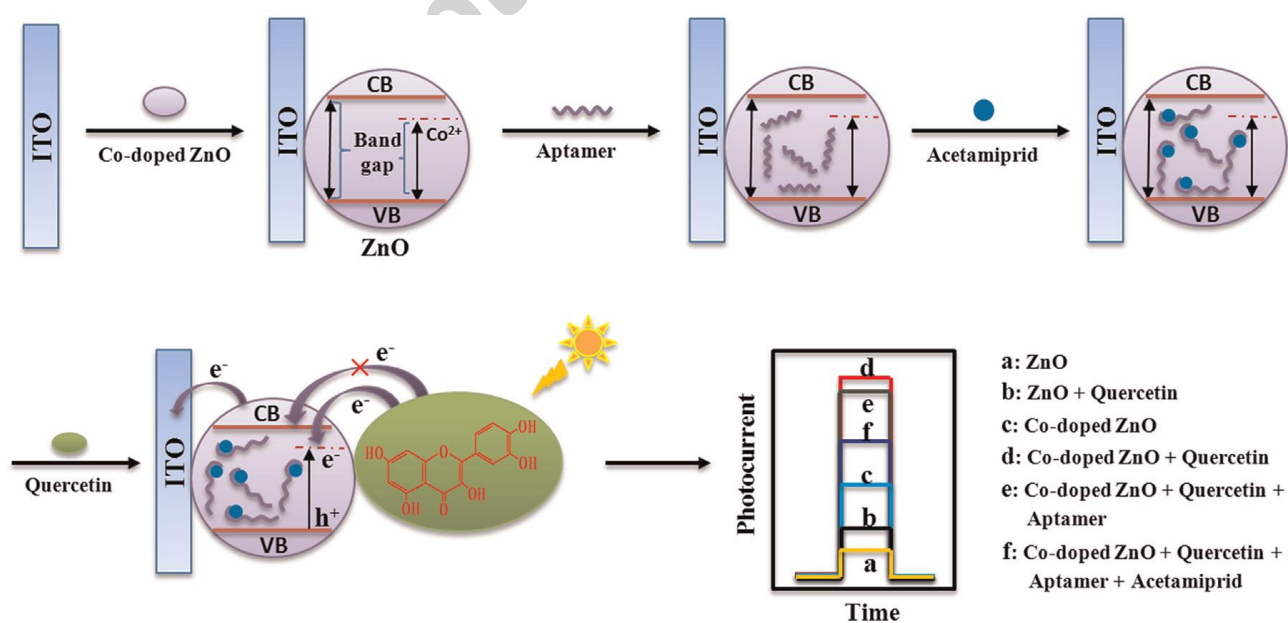


Figure 12

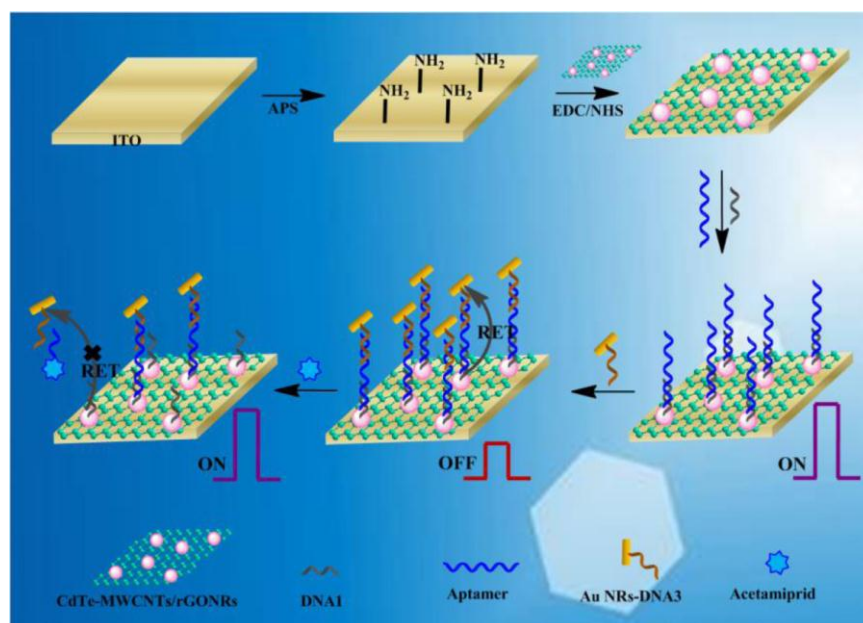


Table captions:

Tables:

Table 1 Available optical based acetamiprid aptasensors.

Detection method	Strategy	LOD	Linear range	References
Colorimetry	GNPs-based colorimetric	5 n mol L ⁻¹	75 nM to 7.5 μ mol L ⁻¹	[38]
Colorimetry	peroxidase-like nanozyme activity of GNPs	0.1 μ mol L ⁻¹	0.1 to 10 μ mol L ⁻¹	[29]
Colorimetry	peroxidase-like activity of hemin-rGO	40 n mol L ⁻¹	100 nM to 10 μ mol L ⁻¹	[41]
Colorimetry	GNPs-based colorimetric	0.4 m mol L ⁻¹	Not reported	[42]
Fluorescence	FRET between ZnS:Mn-Aptamer and MWCNTs.	0.7 n mol L ⁻¹	0 to 150 n mol L ⁻¹	[49]
Fluorescence	FRET between Cy5.5 and QDs	0.02 μ mol L ⁻¹	0.01 μM to 10 μ mol L ⁻¹	[50]
Fluorescence	FRET between NH ₂ -NaYF ₄ :Yb, Ho@SiO ₂ and GNPs	3.2 n mol L ⁻¹	50 nM to 1000 n mol L ⁻¹	[57]
Fluorescence	three nanoparticles for signal amplification	127 p mol L ⁻¹	400 pM to 700 n mol L ⁻¹	[63]
Fluorescence	filter effect of GNPs on the fluorescence of CdTe QDs	7.29 n mol L ⁻¹	0.05 to 1.0 μ mol L ⁻¹	[70]
Chemiluminescence	GNPs morphology effects on CL	62 p mol L ⁻¹	0.8 to 630 n mol L ⁻¹	[67]
RLS	GNPs morphology effects on RLS	1.2 n mol L ⁻¹	0 to 100 n mol L ⁻¹	[69]

Table 2 Available electrochemical based acetamiprid aptasensors.

Detection method	Strategy	LOD	Linear range	References
EIS	GNPs modified electrode	1 n mol L ⁻¹	5 to 600 n mol L ⁻¹	[73]
EIS	Au/MWCNT-rGONR composites modified electrode	17 f mol L ⁻¹	50 f M to 10 μ mol L ⁻¹	[74]
EIS	Silver nanoparticles anchored on nitrogen-doped graphene	0.33 f mol L ⁻¹	0.1 p mol L ⁻¹ to 5 n mol L ⁻¹	[75]
DPV	competitive format	0.09 μ mol L ⁻¹	0.25 to 2.0 μ mol L ⁻¹	[76]
DPV	target-induced release of the redox probe	153 p mol L ⁻¹	0.5 to 650 n mol L ⁻¹	[77]
PEC	Co-doped ZnO diluted magnetic semiconductor nanoparticles	0.18 n mol L ⁻¹	0.5 to 800 n mol L ⁻¹	[79]
PEC	Resonance energy transfer from CdTe quantum dots to gold nanorods	0.2 p mol L ⁻¹	0.5 p mol L ⁻¹ to 10 μ mol L ⁻¹	[80]

Highlights

- acetamiprid is an insecticide that can generate potential health risk of humans.
- aptamers have attracted as a novel sensing elements.
- Nanomaterials have become one of the most interesting sensing materials.
- Recent development in the nano-aptasensing of acetamiprid was reviewed.